Water Remediation Utilizing ISA-TSC and SC Chelating Resins

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Introduction

Semicarbazones and thiosemicarbazones have proven effective water remediation methods for removal of metal ions in aqueous solutions in past research studies.[1] Their ability to extract heavy metals from contaminated bodies of water could prove useful to the field of environmental chemistry. The purpose of this research study is to use ISA-PTSC and ISA-PSC resins for absorbing cadmium out of solution. It is anticipated that both resins will absorb cadmium to some degree. However, based on hard-soft acid base theory, it is anticipated that the ISA-PTSC will be more efficient than the ISA-PSC resin.

Experimental

- ISA-PSC (Figure 2) and ISA-PTSC (Figure 3) ligands were synthesized by reacting isatin-5-sulfonic acid (sodium salt dihydrate) with 4-phenylsemicarbazide or 4-phenylthiosemicarbazide respectively.
- Ligands were gravity filtered and allowed to dry before using.
- Chelating resins were prepared at a 1% by mass loading of the ligand by stirring the anion exchange resin in a solution of the ligand overnight. The chelating resins were gravity filtered and allowed to dry before using.
- A pH 8 buffer solution was made using boric acid (H_3BO_3), 0.1M sodium hydroxide (NaOH), and DI water. The pH was determined to be 8.04.
- A stock solution ($2.7x10^5$ ppb) of cadmium chloride ($CdCl_2$) was made by diluting $CdCl_2$ with the pH 8.04 buffer solution.
- Stock solution was then diluted with pH 8.04 buffer solution to make a reaction solution ($1.7x10^4$), and five calibration standards (3000, 2250, 1500, 750, and 15 ppb).
- Adsorption studies were conducted by a batch method by adding 20-50 mg of the resin to a vial.
- A 1 mL aliquot of the reaction solution was added to each vial and allowed to stir for a specified time period (15 or 30 min, 1, 2, or 4 hours).
- The solutions were filtered through a syringe filter and 0.75 mL of the solution was added to a 15 mL centrifuge tube for analysis and diluted to 5 mL with the pH 8.04 buffer.
- The samples were analyzed for Cd^{2+} concentration via a PerkinElmer Avio 200 ICP-OES.
- Dry weight distribution values (D_w) were calculated according to Equation 1.
- A kinetic study was conducted using the adsorption of the cadmium ion over different time period to see how time impacted adsorption and if equilibrium was established.

$$D_W = \frac{A_o - A_e}{A_e} * \frac{mL}{g}$$

Equation 1: Calculation of dry weight distribution values

A_o = Initial Cd^{2+} concentration
A_e = Concentration of Cd^{2+} in timed samples
mL = volume of Cd^{2+} solution used
g = mass of resin

Results

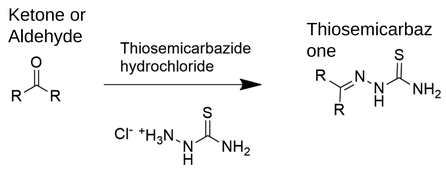

Figure 1: General Synthesis of Thiosemicarbazone

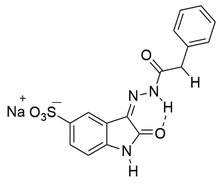

Figure 2: Isatin Sulfonic Acid- Phenyl Semicarbazone (ISA-PSC)

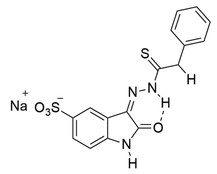

Figure 3: Isatin Sulfonic Acid- Phenyl Thiosemicarbazone (ISA-PTSC)

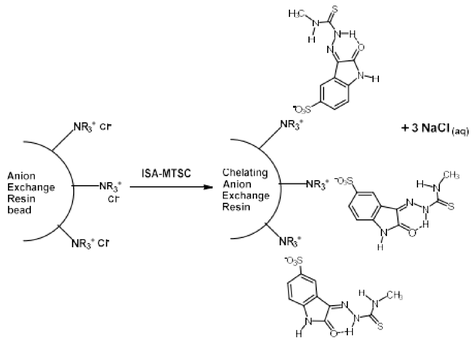

Figure 4: Preparation of Chelating Resin

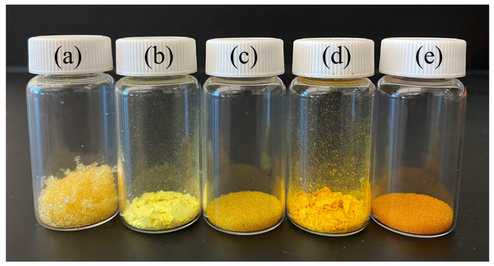

Figure 5: (a) Unmodified resin, (b) ISA-PSC ligand, (c) ISA-PSC resin, (d) ISA-PTSC ligand, (e) ISA-PTSC resin

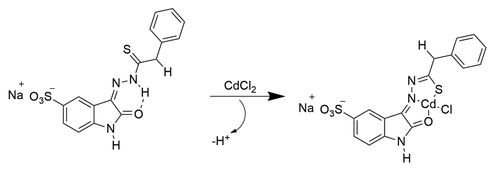

Figure 6: ISA-PTSC-Cd Tridentate Metal-Ligand Complex

Table 1: Cd^{2+} concentration and D_w values for ISA-PSC resins

ISA-PSC		
Time	Concentration Cd (ppb)	D_w
15 min	14175	7.32
30 min	13235	8.32
1 hour	12622	9.86
2 hours	10982	15.5
4 hours	10237	16.8

Table 2: Cd^{2+} concentration and D_w values for ISA-PTSC resins

ISA-PTSC		
Time	Concentration Cd (ppb)	D_w
15 min	8073	30.3
30 min	4405	70.3
1 hour	2292	147
2 hours	1695	241
4 hours	1066	344

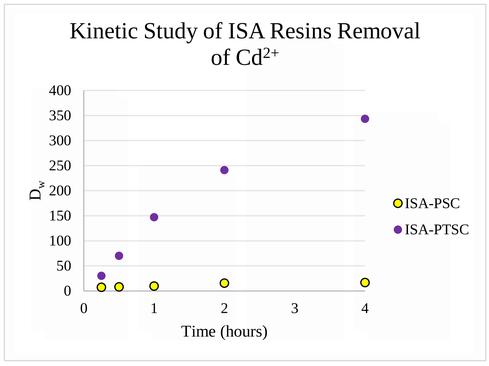

Figure 7: Kinetic study of Cd^{2+} adsorption onto ISA resins

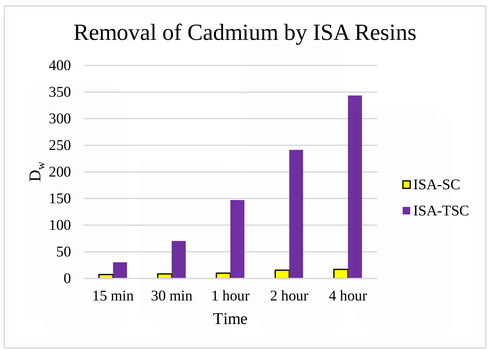

Figure 8: Removal of Cd^{2+} by ISA resins

Discussion

The chelating resins were prepared by displacing a chloride ion from the resin and attaching the ligand by its sulfonic acid moiety as demonstrated in Figure 4. The color change of the resins shown in Figure 5 demonstrated the ligand loading onto the resin.

It was found that the ISA-PTSC complex was significantly more effective than the ISA-PSC complex at removing Cd^{2+} from solution as evidenced by the higher D_w values. It is anticipated the ligand forms a tridentate chelating system with the cadmium ion as shown in Figure 6.

The ISA-PTSC was more effective as a result of the presence of a sulfur atom, opposed to the oxygen atom in the ISA-PSC ligand. According to hard-soft acid base theory, the sulfur acts as a soft base, whereas the oxygen atom on the ISA-PSC, is a hard base. The cadmium ion is a soft acid, making the ISA-PTSC interaction stronger, leading to more effective removal.

Future Work

Further research will be done to examine the effectiveness of both resins to extract the cerium ion (Ce^{3+}) from solution. Since the ISA-PTSC worked better with the cadmium extraction based on the soft sulfur atom, it is anticipated that the ISA-PSC will more effectively remove the cerium from solution. This is because cerium is a hard acid which should form a strong interaction with oxygen atom, which is a hard base. Based on the results from this research study and the interactions between the ISA-PTSC and cadmium solution, it is anticipated that a similar result will emerge from the ISA-PSC and cerium solution.

References

[1] Crook, Amanda J. et. Al., Thiosemicarbazone and Semicarbazone Chelating Resins and Their Potential Use in Environmental Applications. *Separation Science and Technology*. 2012, 47:14-15, 2225-2229, DOI: 10.1080/01496395.2012.697524

[2] Jaishankar, M.; Tseten, T.; Anbalagan, N.; Mathew, B. B.; Beeregowda, K. N. Toxicity, Mechanism and Health Effects of Some Heavy Metals. Interdisciplinary Toxicology 2014, 7 (2), 60–72. https://doi.org/10.2478/intox-2014-0009.

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